

Fast, High-Yielding Syntheses of Silsesquioxanes Using Acetonitrile as a Reactive Solvent

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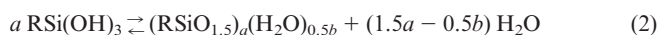
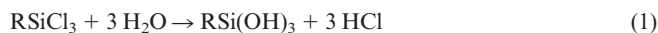
New and efficient methods for the synthesis of cyclopentyl- and cyclohexylsilsesquioxanes are described. In the case of cyclopentylsilsesquioxane, pure trisilanol (*c*-C₅H₉)₇-Si₇O₉(OH)₃ was obtained selectively within 18 h in an isolated yield of 64%. The synthesis of cyclohexylsilsesquioxanes also gives high yields, but it is not selective towards a

particular structural type [main products: (*c*-C₆H₁₁)₆Si₆O₉, (*c*-C₆H₁₁)₆Si₆O₈(OH)₂, (*c*-C₆H₁₁)₇Si₇O₁₀OH and (*c*-C₆H₁₁)₇Si₇O₉(OH)₃]. We discuss the crucial role of acetonitrile as a reactive solvent in these syntheses.

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Introduction

Silsesquioxanes are hybrid inorganic/organic compounds that have an increasing number of applications in the field of catalysis^[1,2] and materials science.^[3,4] In particular, the incompletely condensed silsesquioxanes R₇Si₇O₉(OH)₃ (where R is an organic group, commonly cyclopentyl or cyclohexyl, cf. Figure 1) have been used both as soluble model compounds for silica surface sites and as precursors for active homogeneous catalysts.^[5–9] The synthesis of this silsesquioxane was first reported by Brown and Vogt;^[10] more recently it was optimised and studied in detail by Feher et al.^[11,12] The trisilanol R₇Si₇O₉(OH)₃ [structural coding *a7b3*, cf. Equations (1) and (2)] can be obtained by the slow hydrolytic condensation of the corresponding trichlorosilane RSiCl₃ with acetone as the solvent [Equation (1), Equation (2) with *a* + *b* = 2*n*, where *a*, *b* and *n* are integers (*a* = 1, 2, 3, ...; *b* = 0, 1, 2, 3, ...; *n* = 1, 2, 3, ...) and *b* ≤ *a* + 2].



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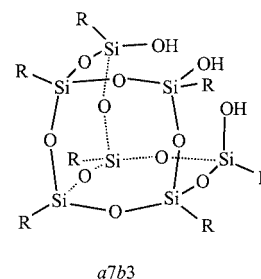


Figure 1. Silsesquioxane *a7b3* [R = cyclopentyl, cyclohexyl]

In the case of R = cyclopentyl, silsesquioxane *a7b3* was the only product of the hydrolytic condensation and was obtained after 3 d of reaction in a yield of 29%.^[12] When R = cyclohexyl, the hydrolytic condensation proceeded more slowly and produced a mixture of three silsesquioxanes: *a6b0*, *a7b3* and *a8b2*.^[11] Silsesquioxane *a7b3* was the main product, but in a low yield (8% after a reaction of 12 weeks).

Recently, we reported a study of the synthesis of silsesquioxanes as precursors for Ti catalysts that are active in the epoxidation of alkenes, which we realised by means of High-Speed Experimentation (HSE) techniques.^[13,14] We investigated the effects of the various parameters that influence the hydrolytic condensation and identified some general trends. Since one of our purposes was to find a faster way to prepare silsesquioxane precursors suitable for active catalysts, the reaction time was set at 18 h, which is a much shorter time than is required usually for the synthesis of silsesquioxanes. The best catalysts were obtained with R = cyclopentyl and cyclohexyl, using acetonitrile as the solvent. In this article, we report a follow-up study of these HSE leads by means of conventional laboratory techniques

with the aim of fully characterising the silsesquioxane products and understanding the role of the solvent.

Results and Discussion

Synthesis of Cyclopentylsilsesquioxanes

The hydrolytic condensation of trichloro(cyclopentyl)silane in acetonitrile in the presence of an excess of water led to the formation of a white precipitate. After a reaction time of 18 h at 50 °C, a crude precipitate was obtained in 54% yield,^[15] which contained mainly silsesquioxane *a7b3* [(*c*-C₅H₉)₇Si₇O₉(OH)₃], as determined on the basis of ²⁹Si NMR and MS analyses. Small amounts of impurities were present in the precipitate, predominantly the cubic, completely condensed silsesquioxane (*c*-C₅H₉)₈Si₈O₁₂ [structural code *a8b0*, cf. Equations (1) and (2)]. If the reaction time was extended from 18 h to 2 weeks,^[14] the yield of precipitated silsesquioxanes was nearly quantitative with the main fraction still being silsesquioxane *a7b3*. The synthesis was further optimised, on the basis of the observation of Feher et al., that the yield of the synthesis of cyclopentylsilsesquioxane *a7b3* in acetone can be significantly improved by heating the reaction mixture under reflux.^[12] Therefore, we modified our synthetic method by increasing the reaction temperature from 50 °C to reflux conditions. This modification led to an increase in the yield to 81% after a reaction time of 18 h and the high selectivity towards silsesquioxane *a7b3* was preserved. Silsesquioxane *a7b3* was then purified by extraction with pyridine^[11,12] and the pure compound (as determined by ²⁹Si NMR spectroscopy, cf. Figure 2) was isolated in an overall yield of 64%, which is a significant improvement over the previously reported yield of 29% after 3 d of reaction.^[12]

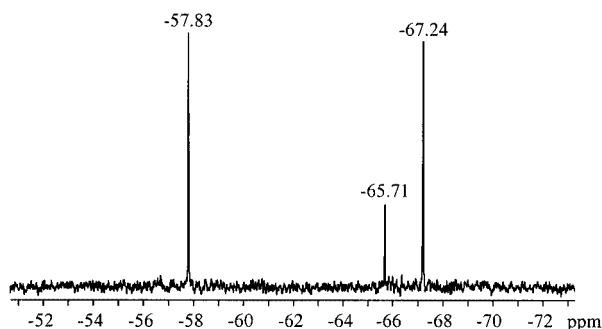


Figure 2. ²⁹Si NMR spectrum of cyclopentylsilsesquioxane *a7b3*

This improved synthetic procedure differs from that reported by Feher et al.^[12] in regard to a number of parameters: the lower initial trichlorosilane concentration, the higher solvent/water ratio and, above all, the nature of the solvent (acetonitrile), which proved to be a dominant parameter that influences the synthesis of silsesquioxanes.^[1,13,14]

After the hydrolytic condensation had proceeded for 18 h under reflux, the reaction mixture separated into two layers: a water phase (bottom) and an acetonitrile phase (top).

This liquid-liquid phase separation is related to the hydrolysis of acetonitrile, a side reaction that is favoured by the presence of an acid [cf. Equation (3)],^[16,17] which, in this case, was the hydrochloric acid produced during the hydrolysis of (*c*-C₅H₉)SiCl₃ [see Equation (3)].



The ammonium chloride obtained is much more soluble in water than it is in acetonitrile, which causes the phase separation [only 0.41 g of ammonium chloride is necessary to induce phase separation of a mixture of water (12.5 mL) and acetonitrile (37.5 mL)]. The preferential solvation of ammonium chloride by water, relative to that of silsesquioxanes or acetonitrile, drives the reaction according to Equation (2) more towards the formation of condensed species. This effect is very pronounced towards the end of the experiment, i.e., when phase separation is actually observed. At the same time, the hydrolysis of acetonitrile in the presence of an acid plays an important role in that the formation of ammonium chloride (partially) neutralises the reaction mixture. A detrimental effect of the acidity of the solution has already been observed in the synthesis of silsesquioxane as Ti catalyst precursors.^[13] Since silsesquioxanes undergo fast hydrolysis/condensation reactions under acidic conditions,^[1] the species formed might be partially decomposed or further condensed before they begin to precipitate from the solution. Partial neutralisation of the reaction mixture could have the effect of slowing down the rates of the hydrolysis/condensation reactions and, thus, favour the precipitation of species that are only poorly soluble in this medium, like the incompletely condensed silsesquioxane *a7b3*.^[18]

A further contributing factor regarding the improved yield when using acetonitrile as the solvent is its higher polarity relative to acetone, the solvent reported in the literature for the synthesis of silsesquioxane *a7b3*.^[12] A highly polar solvent can better stabilise the incompletely condensed species by its interactions with their silanol groups, which, therefore, favours the synthesis of these silsesquioxanes over the completely condensed structures. Moreover, it has been proposed that the activation barrier for the condensation reactions towards the formation of silsesquioxanes is reduced in the presence of a polar molecule and that, therefore, the rate of product formation is increased.^[19,20]

In this context, it is also relevant to note that acetonitrile has a higher boiling point than acetone (82 °C vs. 56 °C). Since the reaction is performed under reflux, the synthesis is accelerated further.

Synthesis of Cyclohexyl Silsesquioxanes

The hydrolytic condensation of trichloro(cyclohexyl)silane in acetonitrile, in the presence of an excess of water, produced a white precipitate in 42% yield^[15] after a reaction time of 18 h at 50 °C. The crude precipitate contained a mixture of silsesquioxane species, as determined by ²⁹Si NMR spectroscopy. The formation of the precipitate was

accelerated by performing the synthesis under reflux, by analogy to the synthesis of cyclopentylsilsesquioxanes. This modification caused an increase of the yield to 79% after a reaction time of 18 h, with the precipitate still being a complex mixture of silsesquioxanes (see Figure 3 for the ^{29}Si NMR spectrum and the MS plot). MS analysis indicated that the silsesquioxanes present in the mixture mainly constituted 6, 7 or 8 siloxane units [$6 < a < 8$, cf. Equations (1) and (2)]. The most-intense peak in the ^{29}Si NMR spectrum ($\delta = -56.72$ ppm, 40% of the crude precipitate)^[21] belongs to the completely condensed silsesquioxane ($c\text{-C}_6\text{H}_{11}$)₆Si₆O₉ (*a6b0*, see Figure 4), which can be separated readily from the incompletely condensed species by extraction with pyridine, in which only the latter silsesquioxanes are soluble.^[11] The main species present in the remaining mixture of incompletely condensed silsesquioxanes were assigned by combining ^{29}Si NMR spectroscopic and MS data: ($c\text{-C}_6\text{H}_{11}$)₆Si₆O₈(OH)₂ (*a6b2*, 11% of the crude precipitate,^[21] see Figure 4), ($c\text{-C}_6\text{H}_{11}$)₇Si₇O₁₀OH (*a7b1*, 29%, see Figure 4) and ($c\text{-C}_6\text{H}_{11}$)₇Si₇O₉(OH)₃ (*a7b3*, 7%, see Figure 1). Silsesquioxane *a7b3* can be separated by precipitation from a THF solution of the incompletely condensed silsesquioxane mixture by the slow addition of acetonitrile, in which it has a very low solubility. Silsesquioxane *a6b2* is, on the other hand, the compound having the highest solubility in acetonitrile among those present in the mixture. Therefore, it can be separated by adding more acetonitrile slowly to the THF/acetonitrile solution, which, thus, induces the precipitation of all the other silsesquioxane structures. The solid obtained after removing silsesquioxanes *a6b2* and *a7b3* still contained a mixture of incompletely condensed silsesquioxanes that have very similar solubilities in many organic solvents and, therefore, resisted all attempts of further purification. The main component of this mixture was assigned to an *a7b1* silsesquioxane structure (two isomers are possible for this silsesquioxane, see Figure 4).

The assignments were confirmed by silylation of the silanol groups of the incompletely condensed silsesquioxanes by means of their reaction with chlorotrimethylsilane ($(\text{CH}_3)_3\text{SiCl}$).^[22] The mixture of incompletely condensed structures obtained after separation of silsesquioxane *a6b0* was treated with an excess of $(\text{CH}_3)_3\text{SiCl}$. The MS analysis of the products of the silylation reaction clearly shows the presence of four main species: disilylated *a6b2*, monosilylated *a7b1*, disilylated *a7b3* and disilylated *a8b2* (Figure 5). The monosilylated *a7b1* was the species present in the highest concentration. On the basis of these experiments, the assignment of *a7b1* as the main incompletely condensed species appears unequivocal. The ^{29}Si NMR spectroscopic peaks belonging to this silsesquioxane *a7b1*, both silylated or not, did not, however, correspond to those of the analogous silsesquioxane reported in the literature.^[11] The peaks corresponding to the silylated *a7b1* reported by Feher were present in the ^{29}Si NMR spectrum only as the second main species. This observation suggests that the two isomers of silsesquioxane *a7b1* (Figure 4) were formed by our synthetic method, with the one known from the literature being the less abundant ($\alpha/\beta = 1:2$). The two isomers differ only in

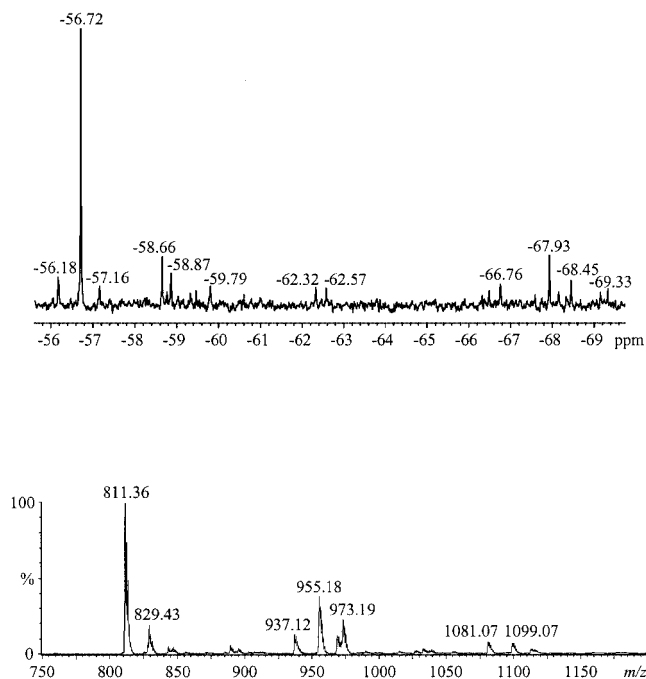


Figure 3. ^{29}Si NMR spectrum (top) and MS plot (bottom) of the cyclohexylsilsesquioxane mixture obtained after the hydrolytic condensation of trichloro(cyclohexyl)silane in acetonitrile

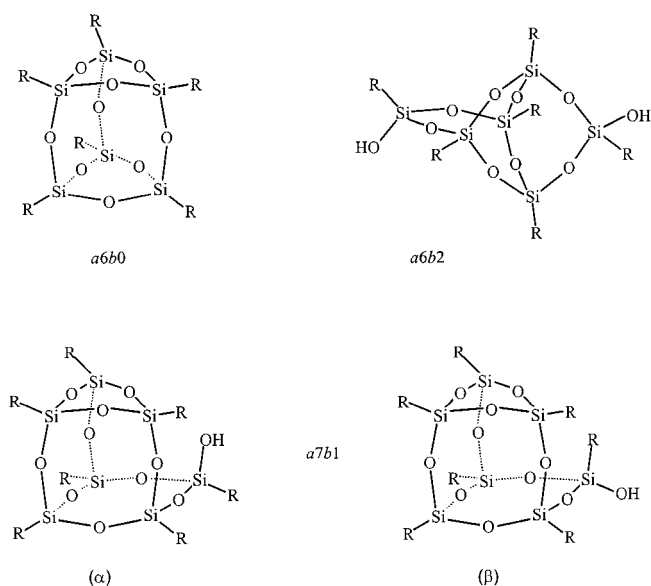


Figure 4. Silsesquioxanes *a6b0*, *a6b2* and *a7b1* (α and β isomers) ($\text{R} = \text{cyclohexyl}$)

the spatial orientations of their silanol groups. They are both possible products of the hydrolytic condensation of trichloro(cyclohexyl)silane, while only the α -isomer of sil-

sesquioxane *a7b1* is obtained by the dehydration of silsesquioxane *a7b3* reported by Feher.^[11]

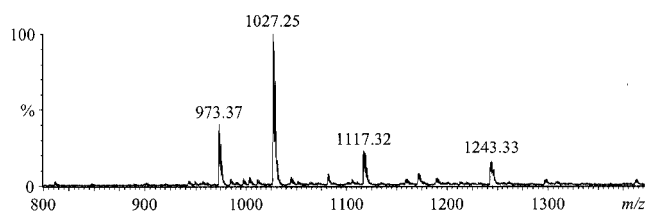


Figure 5. MS analysis of the incompletely condensed cyclohexylsilsesquioxanes, after silylation with $(\text{CH}_3)_3\text{SiCl}$

After hydrolytic condensation for 18 h under reflux and removal of the precipitate, the reaction was left at room temperature for 20 weeks: more white precipitate was formed (additional 10% yield).^[15] The crude product was a mixture of three silsesquioxane species, with some impurities, as determined by ^{29}Si NMR spectroscopy: *a6b0* (21%),^[21] *a6b2* (27%) and *a7b3* (51%). Feher et al. have reported a similar increase in the ratio of silsesquioxane *a7b3* among the products as the reaction time is increased.^[11]

The synthesis procedure described here is the first reported method for obtaining silsesquioxanes *a6b2* and *a7b1* (both isomers) by the hydrolytic condensation of trichloro(cyclohexyl)silane. Cyclohexylsilsesquioxane *a6b2* has been synthesised previously by the acid-mediated cleavage and rearrangement of silsesquioxane *a6b0*.^[23] The α -isomer of cyclohexylsilsesquioxane *a7b1* has been obtained formerly by dehydration of silsesquioxane *a7b3*.^[11] The synthesis also afforded cyclohexylsilsesquioxane *a7b3* in significant yields, although its separation from the rest of the mixture is not straightforward. This new method presents a number of differences from those reported previously,^[11] namely: the solvent (acetonitrile), the lower initial trichlorosilane concentration and the higher solvent/water ratio. Additionally, performing the reaction under reflux caused a noticeable increase in yield of precipitate in our synthesis, while the rate of silsesquioxane formation could not be improved for the reaction reported in literature. Comparing the two synthetic methods, it is evident that the formation of silsesquioxanes is much faster with the new method, albeit less selective. Such an increase in the rate of formation of silsesquioxanes suggests that the conditions for the precipitation of silsesquioxanes are met more readily and for a larger number of different structures. This fact points to the relevance of using acetonitrile as the solvent, in agreement with the situation observed for the synthesis of cyclopentylsilsesquioxanes (vide supra). Analogously, after a reaction time of 18 h under reflux, the hydrolysis of acetonitrile and the consequent formation of NH_4Cl caused a liquid-liquid phase separation of the reaction mixture. To further study the effect of the presence of NH_4Cl , two additional experiments were performed:

1) Some NH_4Cl (0.073 M) was added to the starting mixture and led, after a reaction time of 18 h under reflux, to a silsesquioxane precipitate in a yield of 82%.^[15] ^{29}Si NMR spectroscopic analysis showed that the amount of *a6b0* in-

creased relative to the other (incompletely condensed) silsesquioxanes. Thus, the addition of NH_4Cl not only increased the yield, but also drove the reaction towards the completely condensed species, which confirms the influence that the preferential solvation of NH_4Cl by water has on the silsesquioxane synthesis.

2) The hydrolytic condensation of trichloro(cyclohexyl)silane was performed in acetone (the solvent used by Brown^[10] and Feher^[11]) in the presence of NH_4Cl (0.15 M) as an additive: no precipitate was formed after a reaction time of 18 h under reflux (as is the case when no NH_4Cl is added). This finding indicates that the preferential solvation of NH_4Cl by water alone is not sufficient to accelerate the formation of silsesquioxanes.

The lower selectivity of the synthesis of cyclohexylsilsesquioxanes relative to that of cyclopentylsilsesquioxanes seems to be connected to the nature of the organic group.^[1] The relatively larger steric hindrance of a cyclohexyl unit might account for the formation of the completely condensed silsesquioxane *a6b0*. The Si–O framework of this molecule is more strained than in the case of silsesquioxane *a7b3* and, therefore, its formation might be expected to be unfavourable. On the other hand, the organic groups on the silicon atoms in this structure point away from each other: this arrangement may favour the formation of this molecule for bulkier organic groups, like cyclohexyl. Another effect of the organic group is to influence the solubility of the silsesquioxanes.^[1] Cyclohexylsilsesquioxane *a7b3* has been reported to be more soluble in organic solvents than cyclopentylsilsesquioxane *a7b3*.^[11,12] The lower solubility of the cyclopentyl structure can account for its selective formation as a precipitate.

Conclusions

New methods for the synthesis of cyclopentyl- and cyclohexylsilsesquioxanes have been developed. In both cases, acetonitrile plays a strong role in accelerating the formation of a silsesquioxane precipitate. The influence of the hydrolysis of acetonitrile on the synthesis has been ascertained.

In the case of cyclopentylsilsesquioxanes, the synthesis is very selective towards the formation of structure *a7b3*, which can be obtained in 64% yield after a reaction time of 18 h. This fast and high-yielding method for preparing silsesquioxane *a7b3*, therefore, makes this compound more readily available for its many applications.

In the case of the synthesis of cyclohexylsilsesquioxanes, four silsesquioxane structures were produced in significant yields: *a6b0*, *a6b2*, *a7b1* (both isomers) and *a7b3*. This method offers a facile way to synthesise the silsesquioxane structures *a6b2* and *a7b1*, which are not readily accessible. The lower selectivity of this reaction seems to be connected to the higher solubility of cyclohexylsilsesquioxanes relative to that of cyclopentylsilsesquioxanes.

Experimental Section

General: ^{29}Si NMR spectroscopic characterisation of the silsesquioxanes was performed with a Varian VXR-400S (79.5 MHz, ^1H -

decoupled, 25 °C) and with a Varian Inova-300 (59.6 MHz, ^1H -decoupled, 25 °C); pulse width = 30°; pulse delay = 10 s; ^1H -decoupling during acquisition only. The positions of the silsesquioxanes' peaks in the ^{29}Si NMR spectra are influenced by the solvent in which they are dissolved. Spectra were recorded in THF and CDCl_3 , with TMS as a reference. Mass spectrometric characterisation of the silsesquioxanes was performed with a Micromass Quattro LC-MS using ESI+ and APCI+ as ionisation techniques. Mass spectrometric analysis allows the identification of the number of siloxane units constituting the silsesquioxane structures (i.e., the value of a), but not their level of condensation (i.e., the value of b); this phenomenon is due to the fact that silsesquioxanes can coordinate or lose water molecules during the ionisation process.

Synthesis of Cyclopentyl Silsesquioxanes: Typically, deionised water (37.5 mL) was added carefully into a 500-mL round-bottom flask containing a solution of trichloro(cyclopentyl)silane (97% purity, 5.6 mL, 3.3×10^{-2} mol) in acetonitrile/water (4:1, v/v; 150 mL). This homogeneous solution was then heated to 50 °C or under reflux while stirring vigorously for 18 h; a white precipitate formed. The crude precipitate was dissolved in 20 times its weight of pyridine and stirred overnight. Next, the solution was filtered to remove the insoluble completely condensed species (traces) and poured into an equal volume of ice-cold aqueous HCl (37%); a white precipitate formed. The solid was filtered, carefully washed with water and dried overnight at 45 °C. An NMR spectrum of pure cyclopentylsilsesquioxane *a7b3* was obtained. $^{29}\text{Si}\{^1\text{H}\}$ NMR (THF): δ = -57.83 [s, 3 Si, (c-C₅H₉)SiO(OH)], -65.71 [s, 1 Si, (c-C₅H₉)SiO_{1.5}], -67.24 [s, 3 Si, (c-C₅H₉)SiO_{1.5}] ppm. MS (ESI+, cone voltage = 60 V, THF 78%, CH₃CN 20%, HCO₂H 0.1 M, 2%): m/z (%) = 875.04 [*a7b3* + H]⁺ (100), 839.00 [*a7b3* - 2 H₂O + H]⁺ (41), 897.08 [*a7b3* + Na]⁺ (16), 911.09 [*a7b3* + 2 H₂O + H]⁺ (16), 857.03 [*a7b3* - H₂O + H]⁺ (11).

Synthesis of Cyclohexyl Silsesquioxanes: Typically, deionised water (125 mL) was added carefully into a 1-L round-bottom flask containing a solution of trichloro(cyclohexyl)silane (97% purity, 15 mL, 8.2×10^{-2} mol) in acetonitrile/water (4:1, v/v; 500 mL). This homogeneous solution was then heated to 50 °C or under reflux while stirring vigorously for 18 h.^[24] The crude precipitate formed was dissolved in 20 times its weight of pyridine and stirred overnight. The solution was then filtered to remove the insoluble completely condensed species (*a6b0*) and poured into an equal volume of ice-cold aqueous HCl (37%) to precipitate the incompletely condensed silsesquioxanes. The solid mixture of silsesquioxanes was filtered, carefully washed with water and dried overnight at 45 °C. Silsesquioxane *a7b3* was separated by dissolving the mixture of incompletely condensed species in 5 times its weight of THF and then by slowly layering an equal weight of acetonitrile over the THF solution. Under these conditions, a white precipitate was obtained that mainly constituted silsesquioxane *a7b3*. The remaining solution was partially dried under reduced pressure and more acetonitrile was added slowly until a precipitate deposited. The solid was separated by filtration and the solution dried under reduced pressure to afford silsesquioxane *a6b2*. The silylation of the mixture of incompletely condensed silsesquioxanes was performed by adding chlorotrimethylsilane (200 μL) to a solution of the silsesquioxanes (0.3 g) in toluene (30 mL) and triethylamine (1.5 mL). The turbid solution was stirred overnight at room temperature. Next, the solvent and triethylamine were evaporated under reduced pressure to afford a white solid. The solid was extracted with pentane, the solution was filtered to remove the insoluble (C₂H₅)₃N·HCl and then concentrated under reduced pressure to give a solid containing the silylated silsesquioxanes. $^{29}\text{Si}\{^1\text{H}\}$

NMR: *a6b0* (THF): δ = -56.72 [s, 6 Si, (c-C₆H₁₁)SiO_{1.5}] ppm; *a6b2* (THF): δ = -57.16 [s, 2 Si, (c-C₆H₁₁)SiO(OH)], -62.32 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}], -62.57 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}] ppm; (CDCl_3): δ = -55.20 [s, 2 Si, (c-C₆H₁₁)SiO(OH)], -61.72 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}], -61.92 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}]; *a7b1* (THF): δ = -56.18 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -58.66 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}], -58.87 [s, 1 Si, (c-C₆H₁₁)SiO(OH)], -66.76 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -67.93 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}] ppm; (CDCl_3): δ = -56.23 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -57.95 [s, 1 Si, (c-C₆H₁₁)SiO(OH)], -58.58 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}], -66.82 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -67.66 [(s, 2 Si, (c-C₆H₁₁)SiO_{1.5})] ppm; silylated *a7b1* isomers (CDCl_3): (α): δ = 9.06 [s, 1 Si, (CH₃)₃SiO_{0.5}], -56.32 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -59.02 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}], -66.67 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -68.74 [s, 1 Si, (c-C₆H₁₁)SiO[OSi(CH₃)₃]], -68.83 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}] ppm; (β): δ = 8.20 [s, 1 Si, (CH₃)₃SiO_{0.5}], -56.28 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -58.70 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}], -66.89 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -67.35 [s, 1 Si, (c-C₆H₁₁)Si[OSi(CH₃)₃]], -68.14 [s, 2 Si, (c-C₆H₁₁)SiO_{1.5}] ppm; *a7b3* (THF): δ = -59.79 [s, 3 Si, (c-C₆H₁₁)SiO(OH)], -67.86 [s, 1 Si, (c-C₆H₁₁)SiO_{1.5}], -69.33 [s, 3 Si, (c-C₆H₁₁)SiO_{1.5}] ppm. MS of crude precipitate (APCI+, cone voltage = 15 V, CH₂Cl₂; see Figure 3), for $a = 6$: m/z (%) = 811.36 [*a6b0* + H]⁺ (100), 829.43 [*a6b2* + H]⁺ (20); for $a = 7$: m/z (%) = 937.12 [*a7b1* - H₂O + H]⁺ (14), 955.18 [*a7b1* + H]⁺ (38), 973.19 [*a7b3* + H]⁺ (23); for $a = 8$: m/z (%) = 1081.07 [*a8b0* + H]⁺ (8), 1099.07 [*a8b2* + H]⁺ (7); silylated incompletely condensed silsesquioxanes (APCI+, cone voltage = 15 V, toluene/acetonitrile, 2:1, few drops of CH₃CO₂H; see Figure 5): m/z (%) = 973.37 [disilylated *a6b2* + H]⁺ (40), 1027.25 [monosilylated *a7b1* + H]⁺ (100), 1117.32 [disilylated *a7b3* + H]⁺ (22), 1243.33 [disilylated *a8b2* + H]⁺ (15).

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